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(19) (CA) # CANADIAN PATENT

(54) HEAT RESISTANT ALLOY FOR CARBURIZATION RESISTANCE

(70) Bagnoli, Donald L. and Ciuffreda, Anthony R., U.S.A.

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ABSTRACT OF THE DISCLOSURE

Catastrophic carburization of metal furnace tubes which take place when heating hydrocarbons is minimized by using an alloy which when oxidized forms a protective manganese and chromium oxide scale. In practice this is done by contacting the hydrocarbons with a heated metal surface that has an adherent layer of manganese and chromium oxide on the metal surface which is in contact with the hydrocarbon. The protective scale of manganese and chromium oxide is formed on the surface of an alloy consisting essentially of chromium, iron and nickel as well as manganese, by adjusting the nickel content of the alloy to the range of 36 to 38% and the manganese content of the alloy from 1.25 to 2.0%, forming the alloy into a metal surface, and thereafter, treating the metal surface with steam at elevated temperatures for a time sufficient to oxidize manganese and chromium present in the alloy and form a protective scale of manganese and chromium oxide.

This invention relates to a technique for minimizing carburization of furnace tubes exposed to hydrocarbons under pyrolysis and reforming conditions.

In processes for the controlled pyrolytic decomposition of hydrocarbons, typically, the hydrocarbon is decomposed at high temperatures under varying pressure conditions in the presence of predetermined amounts of steam.

It has been well recognized that the above-mentioned cracking and reforming processes when conducted in the presence of certain metals and metal alloys often lead to excessive deposition of carbon. These carbon deposits reduce the size of the furnace tubes with concomitant problems of plugging, and also affect the strength of the metal furnace tubes resulting in structural failure of the metal tubes. In such instances such failure is frequently referred to as catastrophic carburization of the metal.

It is known for example that iron surfaces will have a catalytic effect upon the pyrolysis of hydrocarbons, promoting carbon formation. The carbon formed is absorbed or diffused into the metal resulting in the structural failure of the metal. Consequently, numerous techniques have been proposed for avoiding such catastrophic carburization of metal tubes by alloying the iron and/or by forming protective coatings of an oxide on the surface of the metal to be contacted with the hydrocarbon under the reforming or pyrolysis conditions. None of these techniques have provided a complete panacea and there still is a commercial interest in

preventing carburization of furnace tubes.

According to the present invention, there is provided a method of heating hydrocarbon carbons in contact with metal surfaces under conditions which normally would cause difficulties due to carburization of the metal surfaces which comprises contacting the hydrocarbons of the metal surface containing adherent oxide layer of manganese and chromium, whereby heat is passed from the metal surface to the hydrocarbon without significant carburization of the metal.

Thus, in one aspect the present invention contemplates a method of rendering metal surfaces exposed to hydrocarbons under pyrolysis and reforming conditions resistant to carburization by providing on such metal surfaces in contact with the hydrocarbons an adherent layer of manganese and chromium oxide.

In yet another aspect of the present invention, an adherent layer of manganese and chromium oxide is formed on a metal alloy surface by oxidizing a nickel-chromium-iron alloy that has at least 36% nickel and from 1.25% to 2.0% manganese.

The present invention can be carried out for example by passing a hydrocarbon through a heating means having one or more tubes or conduits which are heated directly or indirectly to transfer heat to the hydrocarbon. The metal surfaces to be used in accordance with this invention should have an adherent coating of manganese and chromium oxide.

In a particularly preferred embodiment of the present invention the metal tubes are formed from an

alloy consisting essentially of chromium, nickel and iron and having at least 1.25% manganese and at least 36% nickel. For example, the alloy may have from 36 to 38% nickel, from 23 to 27% chromium, and from 1.25% to 2% manganese. Indeed such an alloy when contacted with steam at elevated temperatures for a time sufficient to oxidize some of the manganese present in the alloy results in the formation of an adherent protective coating of manganese and chromium oxide which is resistant to carburization. For example, the metal surfaces are pretreated with steam at temperatures in the range of 500°F. to about 2000°F., and preferably at about 1500°F. for from about 24 hours to about 96 hours, such as about 72 hours.

Equally important in providing an adequate protective coating of manganese and chromium oxide on the surface of the metal is the grain structure of the contact surface. It has been discovered that with furnace tubes, for example, the interior contact surface should be made up of equiaxed grain structure. Basically the grain structure is achieved by casting the alloy into a tube and controlling the thermal gradient during solidification. Any other technique known in the art for controlling grain structure can be employed.

The invention will be better understood by reference to the following examples and demonstrations.

<u>EXAMPLE 1</u>

A series of tubes having a 4-inch inside diameter were installed in a furnace and were pretreated with steam at 1450°F. for 72 hours.

Hydrocarbons were fed through the tubes in contact with the interior surfaces of the metal. The metal tubes were maintained at temperatures generally of the order of 1900°F. In these tests, two alloy compositions were used. The alloy compositions are set forth in Table I below.

TABLE I

	Alloy 1	Alloy 2
Carbon, %	0.4-0.5	0.43
Manganese, %	1.09	1.30
Silicon, %	1.01	1.10
Chromium, %	28.0	23.5
Nickel, %	19.0	37.0
Molybdenum, %	0	1.89
Iron, %	Balance	Balance

At the end of 30,000 hours on stream the furnace tubes were physically inspected. Those tubes of alloy 1 were, at least in some instances, carburized as much as 80% and had as little as 2/3 of an effective wall thickness remaining. Those of alloy 2 were effectively protected against carburization. Magnetic readings of the tubes of both alloy 1 and alloy 2 showed that the protected regions were predominantly oxides of manganese and chromium whereas the unprotected areas were predominantly oxides of iron.

In a more detailed analysis performed with a microprobe analyzer, it was surprisingly discovered that a continuous layer of manganese oxide was lying outside the chromium oxide layer and close to the surface and the highly protected layers. Indeed, in

alloy 2 the thickness of the manganese oxide scale was about 10 times greater than the amount of manganese oxide scale in alloy 1.

Apparently, a nickel content, in a nickel-chromium-iron alloy, of greater than 36% and a manganese content of greater than 1.25% is necessary to provide a good protective scale of manganese and chromium oxide in the interior surface of the furnace tube.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for heating hydrocarbons by contact with heated metal surfaces containing nickel and iron under conditions which are likely to result in carburization of the metal, characterized by contacting said hydrocarbons with a heated metal surface that has an adherent layer of manganese and chromium oxide on the metal surface which is in contact with the hydrocarbon, whereby the metal is protected against carburization and heat is passed from the metal to the hydrocarbon.

2. The method of claim 1 wherein said hydrocarbon is contacted with said metal surface at an initial temperature in the range of about 1700°F to 2000°F.

3. The method of claim 1 wherein the metallic surface comprises the inner walls of heat exchanger tubes suitable for heating said hydrocarbon.

4. A method of forming a protective scale of manganese and chromium oxide on the surface of alloy consisting essentially of chromium, iron and nickel as well as manganese characterized by:

(1) adjusting the nickel content of the alloy to the range of 36 to 38% and the manganese content of the alloy from 1.25 to 2.0%;

(2) forming the alloy into a metal surface; and

(3) thereafter, treating the metal surface with steam at elevated temperatures for a time sufficient to oxidize manganese and chromium present in the alloy and form a protective scale of manganese and chromium oxide.

5. The method of claim 4 wherein the metal is treated with steam at temperatures in the range of 500°F to 2000°F for at least about 24 hours.

6. The method of claim 4 wherein the metal is treated with steam at a temperature of about 1450°F for about 72 hours.